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Alkaline peroxide treatment of ECF bleached softwood kraft pulps. Part 1. Characterizing the effect of alkaline peroxide treatment on carboxyl groups of fibers

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Abstract

The influence of alkaline peroxide treatment has been characterized on elementally chlorine-free (ECF) bleached softwood (SW) kraft pulp. The results indicate that fiber charge increased with an increase in peroxide charge: a maximum fiber charge increment of 16.6% was obtained with 8.0% more peroxide charge on oven-dried (o.d.) pulp at 60.0°C. Two primary bleaching temperatures of 60.0°C and 90.0°C were investigated during peroxide treatment. Copper number decreased for peroxide charges of 0.5% and 1.0% at 60.0°C and 90.0°C, respectively, then increased with increasing peroxide charge. Both fiber charge and copper number approached constant values when 4.0% or higher peroxide charge was applied. Peroxide treatment on a bleached kraft pulp at 90.0°C resulted in lower fiber charge and lower intrinsic viscosity compared to treatment at 60.0°C. Sodium borohydride ($NaBH_4$) pretreatment was able to protect the fibers from being degraded during peroxide bleaching. Fiber charge and copper number were compared after peroxide treatment of ECF bleached kraft pulp to $NaBH_4$-reduced ECF bleached kraft pulp. The results indicate that the carbonyl group content of fibers is favorable for improving fiber charge after peroxide treatment.

Keywords: carbonyl; carboxyl; copper number; fiber charge; peroxide; sodium borohydride; tensile strength; viscosity.

Introduction

Elementally chlorine-free (ECF) and totally chlorine-free (TCF) bleaching technologies frequently include bleaching steps with oxygen, ozone, and peroxide. It is well known that hydrogen peroxide brightens mechanical pulp, delignifies kraft pulp, and increases the brightness of bleached chemical pulp and secondary (recycled) fibers (Stevens and Hsieh 1997; Ni et al. 2001; Smook 2002). The fiber charge of modern kraft pulp is largely due to the dissociation of carboxyl groups in the papermaking process (Sjöström 1989). This property can be subdivided into bulk fiber charge and surface charge (Lloyd and Horne 1993). Generally, the bulk fiber charge is measured by conductometric titration (Katz et al. 1984; Lloyd and Horne 1993). Recently, Bohrn et al. (2006) developed a method that can detect the carboxyl content in cellulosic materials by fluorescence labeling with 9*H*-fluoren-2-yl-diazomethane (FDAM). Fiber charge influences several key physical properties, including the swelling of wet fibers, fiber flexibility, fiber-fiber bonding and refinability (Scallan and Grignon 1979; Lindström and Carlsson 1982; Katz and Scallan 1983; Engstrand et al. 1991; Zhang et al. 1994; Barzyk et al. 1997; Laine and Stenius 1997; Pan 2004; Dang et al. 2006). Many of the interactions between soluble and particulate fractions of papermaking furnish are based on charge, and therefore fiber charge plays a pivotal role in papermaking (Lloyd and Horne 1993; Sanders and Schaefer 1995; Isogai et al. 1997). The ability of hydrogen peroxide to enhance the fiber charge of ECF bleached pulps has not been fully explored or exploited. Toven (2003) studied the effect of bleaching processes for chemical pulp on fiber charge and reported that a (P+O)-stage has the potential to increase fiber charge for D(E+O)Q and D/Z(E+O)Q kraft pulps. Zhang et al. (2005) studied a peroxide stage for fully bleached pulps. The authors demonstrated that it is easy to enhance the final charge by 10–25%, which results in improved sheet tensile strength and stiffness properties.

Hydrogen peroxide oxidizes polysaccharides, giving rise to the formation of carboxylic groups, which belong typically to arabinoic, erythronic, glucuronic, and dicarboxylic acids. Carbonyl groups also arise (Godsay and Pearce 1984; Sjöström 1993). Carbonyl groups in pulps can be reduced with sodium borohydride ($NaBH_4$) under caustic conditions (Giertz and McPherson 1956; Schmidt et al. 1995). Carbonyl groups of fibers initiate chain scission in alkaline medium by a β-glucoxy elimination reaction (Gratzl 1987). $NaBH_4$ treatment for fibers has frequently been studied to improve the performance of peroxide bleaching and produce high-brightness pulp (Sjöström and Eriksson 1968; Ni et al. 2001; Wang et al. 2004), and obtain better selectivity of the bleaching process, including oxygen bleaching and ozone bleaching (Odermatt et al. 1998; Cardona-Barrau and Lachenal 2001).

It has been reported that the carbonyl groups in fibers are present as hydrates and/or hemiacetals/hemiketals, in addition to aldehyde and ketone forms (Potthast et al. 2005). There are a few conventional approaches to determine the amount of cellulosic carbonyl groups. Copper number measurement is used to estimate the quantity of carbonyl groups of bleached pulp (Tappi standard 1992c). The reaction mechanism for this protocol depends on copper(II) salts that are reduced by reductive groups in fibers, with the resulting Cu(I) determined titrimetrically.

Measurement of carbonyl groups is also possible by the oxime (Klemm et al. 1998), hydrazine (Albertsson and Nordung 1967), and cyanohydrin methods (Lewin and Epstein 1962). A new approach is the determination of carbonyl groups in cellulosics by fluorescence labeling (Röhrling et al. 2002a,b; Potthast et al. 2003). This methodology is called CCOA, since the marker used is carbazole-9-carbonyloxyamine. Comparison of results obtained by the CCOA and copper number methods revealed a linear relationship between them (Röhrling et al. 2002b).

In this study the effects of peroxide bleaching of ECF bleached softwood kraft pulp on fiber charge and carbonyl group content were studied. We also investigated the effect of $NaBH_4$ pretreatment of bleached kraft pulps prior to peroxide treatment to clarify the role of carbonyl groups in the course of carboxyl group formation during subsequent peroxide treatment.

Materials and methods

Materials

ECF bleaching of pulp employed a D(E+O+P)D bleaching sequence. Basic pulp properties included Tappi brightness of 84.5, intrinsic viscosity of 672 ml g^{-1}, and carboxyl group content of 3.98 mmol 100 g^{-1} o.d. pulp. The pulp was thoroughly washed with distilled water until the effluent pH was neutral, pressed to approximately 30.0% consistency, and stored at 2°C prior to use. All chemicals used in this study were purchased from Aldrich, JT Baker, and Fisher as analytical grade and used as received.

Alkaline peroxide treatment

An ECF bleached softwood kraft pulp was bleached with alkali peroxide in a sealed plastic bag placed in a water bath. All bleaching studies were conducted at 10.0% pulp consistency for a bleaching time 2.0 h and with a 2.0% charge of NaOH. The pulp mixture was vigorously mixed with a glass rod initially and then manually kneaded every 15 min during the reaction. Peroxide charges of 0.5%, 1.0%, 2.0%, 4.0%, and 8.0% were examined at bleaching temperatures of 60.0 and 90.0°C. Another set of peroxide treatments using a 2.0% peroxide charge were performed at a series of temperatures from 40.0°C to 90.0°C.

Sodium borohydride treatment

ECF bleached kraft pulp was treated with $NaBH_4$ in a sealed plastic bag placed in a 60.0°C water bath for 2.0 h. The caustic charge was 2.0% NaOH and the $NaBH_4$ charge was 0.5%, both based on o.d. pulp. The slurry consistency was 10.0%.

Carboxyl group content and surface charge of pulp fibers

The carboxyl group content, usually referred to as fiber charge, was determined by conductometric titration (Katz et al. 1984; Lloyd and Horne 1993) as reported in detail previously (Dang et al. 2006). Experiments were conducted in duplicate and the results had an error of less than ±3%.

Copper number of pulp fibers

Copper number, which was measured according to Tappi standard (1992c) T 430, is defined as the number of grams of metallic copper (as Cu_2O) resulting from the reduction of $CuSO_4$ by 100.00 g of pulp fibers. The copper number of each sample was measured in duplicate, with an error of less than ±5%.

Analysis of paper physical properties

Handsheets were prepared according to Tappi standard (1992a) T205. Tensile strength (Tappi standard 1992d T494) was measured with error less than ±5%. Handsheet caliper (Tappi standard 1992b T411) was measured to determine the density of the handsheets. The intrinsic viscosity was determined according to ASTM standard (2003) D-1795-96. The typical error for intrinsic viscosity is ±5 ml g^{-1} of the average number.

Results and discussion

In our preliminary study (Zhang et al. 2005) and that of Toven (2003) on peroxide bleaching of fully bleached pulps, it has been reported that increased fiber charge results in enhanced swelling of fibers, and better tensile strength and stiffness (Zhang et al. 2005). In the present paper, alkaline peroxide treatment of ECF bleached pulp was investigated in terms of the fiber charge and carbonyl group content.

Effect of peroxide charge on fiber charge

ECF bleached softwood kraft pulp was subjected to alkaline peroxide treatment with a series of peroxide charges from 0% to 8.0%. The other parameters of these experiments were 2.0% NaOH, treatment time of 2.0 h, 10.0% consistency, and temperatures of 60.0 and 90.0°C. Figure 1 shows the effect of peroxide treatment on fiber charge of the treated ECF bleached SW kraft pulp.

The results in Figure 1 indicate that fiber charge was increased by alkaline peroxide treatment up to a peroxide charge of 4.0%, after which it remained approximately constant. The maximum increase in fiber charge achieved was 16.6% for peroxide treatment at 60.0 and 90.0°C. It is obvious that an elevated temperature of 90.0°C was detrimental to fiber charge development. The influence of temperature was further studied in the range 40.0–90.0°C with 2.0% NaOH, 2.0% H_2O_2, 10.0% consistency, and 2.0 h of treatment (Figure 2).

Based on the data, we suggest that the optimal temperature for alkaline peroxide treatment in terms of fiber charge development is between 60.0°C and 70.0°C. A low temperature does not provide enough energy to activate the peroxide oxidizing power necessary for fiber charge formation. Too high a temperature may lead to a high peroxide decomposition rate, i.e., to another limiting

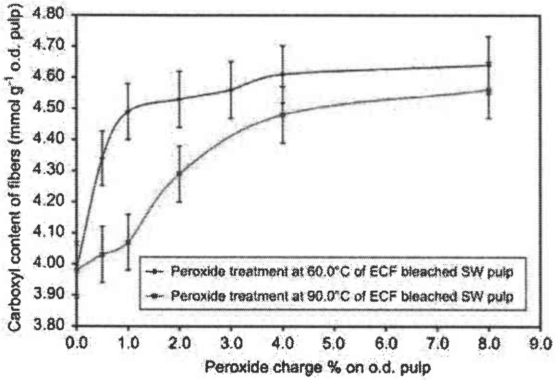

Figure 1 Relation between peroxide charge on o.d. pulp and fiber charge after ECF bleached SW kraft pulp was treated with 2.0% NaOH for 2.0 h at temperatures of 60.0°C and 90.0°C.

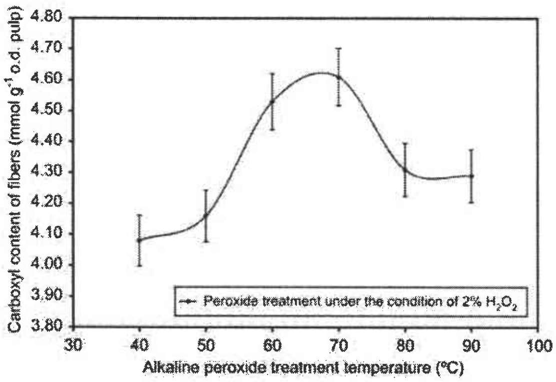

Figure 2 Relation between the temperature of alkaline peroxide treatment and fiber charge after ECF bleached softwood kraft pulp was treated with 2.0% NaOH and 2.0% H_2O_2 (o.d. pulp), 10.0% consistency for 2.0 h.

factor for fiber charge formation (Stevens and Hsieh 1997; Lapierre et al. 2003).

Effect of peroxide charge on intrinsic viscosity

Intrinsic viscosity is related to the molecular weight of the carbohydrates present. A lower viscosity is an indication of lower strength of pulp fibers. Cellulose and hemicelluloses are readily attacked during alkaline oxygen delignification and peroxide bleaching. Hydroxyl radicals, the strongest one-electron oxidants in aqueous media, are responsible for cellulose degradation (Ek et al. 1989; McGrouther et al. 2000).

Data on intrinsic viscosity are summarized in Figure 3 and show that the intrinsic viscosity decreased with increasing peroxide charge. As for the temperature effect, the intrinsic viscosity was lower after peroxide treatment at 90.0°C than for treatment at 60.0°C. This observation is in accordance with literature reports (Stevens and Hsieh 1997).

Effect of fiber charge on paper tensile strength

It is well established that higher carboxyl group content leads to enhanced paper strength (Engstrand et al. 1991;

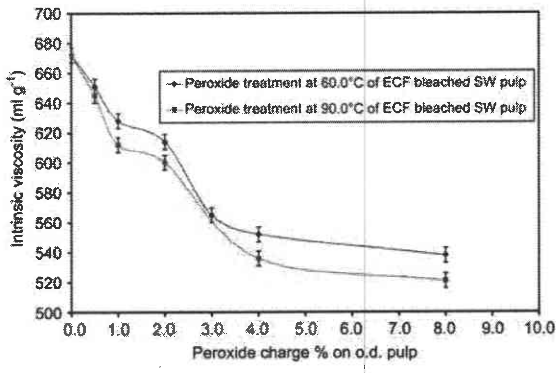

Figure 3 Relation between peroxide charge on o.d. pulp and intrinsic viscosity of fibers after ECF bleached softwood kraft pulp was treated with 2.0% NaOH for 2.0 h at 60.0°C and 90.0°C.

Zhang et al. 1994; Barzyk et al. 1997; Korpela 2002; Pan 2004). Peroxide bleaching is usually the final step in a sequence before refining. Refining improves the final tensile strength. However, it has also been found that grafting with carboxymethyl cellulose (CMC) has the potential to replace the refining operation and its application leads to better paper properties than PFI refining, e.g., in terms of the relationship between tensile strength and light scattering coefficient (Laine et al. 2003). In this study, unrefined pulp was modified by peroxide treatment, which led to improved fiber charge. The effect of the improved fiber charge on refining will be described in a forthcoming paper (Dang et al. 2007). Pulp fibers treated with peroxide at 60.0°C in this study were selected to investigate the influence of improved fiber charge on the tensile strength of the final paper (Table 1).

The tensile index of the untreated ECF bleached pulp was 32.8 Nm g^{-1}. The fiber charge of ECF bleached pulp did not change for 2.0% NaOH treatment. However, the tensile strength increased after 2.0% NaOH treatment to a value of 34.9 Nm g^{-1}. This result can be explained by the increased swelling properties of fibers after alkali treatment (Grignon and Scallan 1980; Rajulu et al. 2003). Moreover, swelling can lead to higher tensile strength (Toven 2003). The data in Table 1 indicate that tensile strength improved with increasing fiber charge after alkaline peroxide treatment. The tensile index of the pulp after

Table 1 Tensile index of ECF bleached softwood pulp after alkaline peroxide treatment at 60.0°C, 2.0% NaOH, 2.0 h and 10.0% consistency.

Peroxide charge (%)	Carboxyl group content (mmol 100 g^{-1})	Tensile index (Nm g^{-1})
Untreated ECF bleached SW pulp	3.98	32.8
0.0 (alkaline extract)	3.98	34.9
0.5	4.34	35.8
1.0	4.49	36.0
2.0	4.53	36.2
3.0	4.56	36.2
4.0	4.61	36.3
8.0	4.64	36.5

Data are based on oven-dried pulp.

alkaline treatment increased by 6.4% compared to the control, while the maximum value increased by 11.3% after 8.0% peroxide treatment. However, alkaline treatment did not change the carboxyl group content, which is of primary importance to retention of wet-end chemicals. The density was in the region of 0.426 ± 0.011 g cm^{-3} and did not show correlation between the control and the peroxide-treated samples. Obviously, the increase in tensile index for the sample with enhanced fiber charge did not relate to the change in sheet density.

Effect of peroxide charge on copper number

Figure 4 shows that the pulp copper number decreased when the peroxide charge was low, but increased when the peroxide charge was elevated to 0.5% (at 60.0°C) and 1.0% (at 90.0°C). It is clear that there is an optimal peroxide charge between 0.5% and 1.0% at which carbonyl groups could be removed. This contributes to an increase in brightness stability. At high peroxide charges, new carbonyl groups are generated, leading to an increase in copper number. The copper number reached a constant value at peroxide charge of 4.0% (Figure 4). The coincidence of maximum fiber charge and copper number at a peroxide charge of 4.0% is remarkable. We suggest that there is a limit to peroxide oxidation of cellulose fibers with respect to carbonyl and carboxyl group formation. Peroxide charges of 4.0% and higher showed no further change in carbonyl and carboxyl group content.

Effect of carbonyl groups of fibers on subsequent peroxide treatment

ECF bleached SW kraft pulp was treated with $NaBH_4$ (Figure 5). The carbonyl group content decreased to zero after treatment with 0.5% $NaBH_4$, which did not affect the fiber charge.

The original pulp fiber was reduced with 0.5% $NaBH_4$ and the reduced fibers were then bleached with alkaline peroxide at charges of 0.5–8.0% peroxide based on o.d. pulp. The parameters during alkaline treatment were 2.0% NaOH (based on o.d. pulp), 60.0°C, 10.0% consistency and 2.0 h.

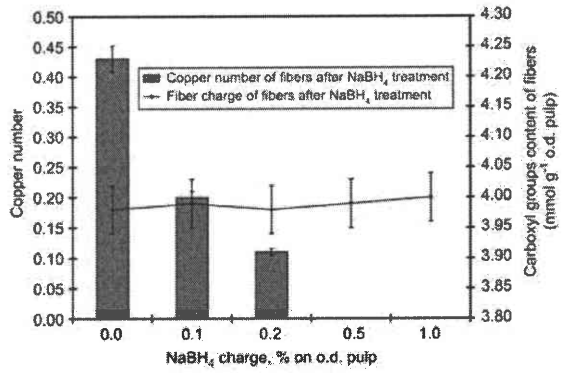

Figure 5 The relationship between sodium borohydride addition, copper number, and fiber charge after fibers were treated with 2.0% NaOH for 2.0 h at 60.0°C with different charges of sodium borohydride.

Based on these experiments, results for peroxide treatment on $NaBH_4$-reduced ECF bleached pulp were compared to those for peroxide treatment of original ECF bleached pulp. Results were compared for intrinsic viscosity (Figure 6), fiber charge (Figure 7) and copper number (Figure 8).

Peroxide bleaching of $NaBH_4$-reduced pulps resulted in higher intrinsic viscosity compared to the control (with no reductive pretreatment) (Figure 6). This is probably due to $NaBH_4$ reduction of carbonyl groups, which decreases the chelating power and helps to remove heavy metals (Odermatt et al. 1998; Cardona-Barrau and Lachenal 2001).

Figure 7 compares the fiber charge after peroxide treatment for original ECF bleached kraft pulp and $NaBH_4$-reduced samples. The best fiber charge improvement is 5.53%, which is much lower than for the original fibers after peroxide treatment (16.6%). Copper numbers for the two types of pulp after peroxide treatment are illustrated in Figure 8. The maximum increase in copper number after peroxide treatment was 0.19 units for the reduced pulp and 0.28 for the original pulp. At 0.5% peroxide charge on the reduced pulp (i.e., the pulp without carbonyl groups) the copper number and carboxyl group content did not increase at all. However, for the same

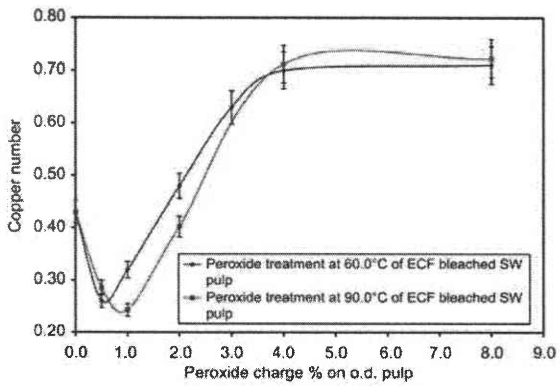

Figure 4 Relation between peroxide charge on o.d. pulp and copper number of ECF bleached softwood kraft pulp fibers treated with 2.0% NaOH for 2.0 h at 60.0°C and 90.0°C.

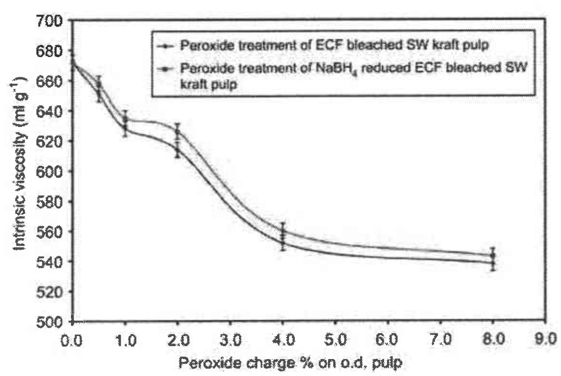

Figure 6 Comparison of the intrinsic viscosity after peroxide treatment of original ECF bleached kraft pulp with $NaBH_4$-reduced ECF bleached kraft pulp.

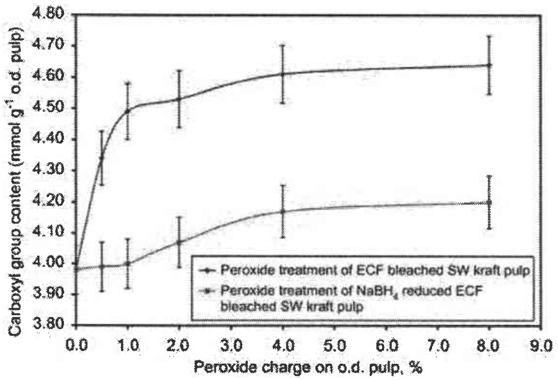

Figure 7 Comparison of the fiber charge after peroxide treatment of original ECF bleached kraft pulp with $NaBH_4$-reduced ECF bleached kraft pulp.

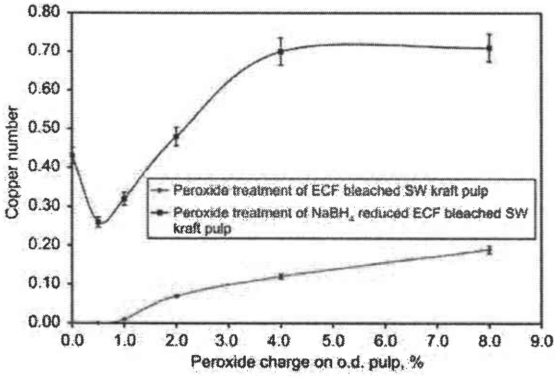

Figure 8 Comparison of the copper number after peroxide treatment of original ECF bleached kraft pulp with $NaBH_4$-reduced ECF bleached kraft pulp.

peroxide charge on the original pulp, the copper number decreased from 0.43 to 0.26 and the carboxyl group content increased by 9.1%. Accordingly, virgin pulp carbonyl groups are the source of the increase in carboxyl groups after peroxide treatment.

Conclusions

Treatment of an ECF bleached kraft pulp with alkaline peroxide at 60.0°C increased the fiber charge by 16.6% at a peroxide charge of 8.0% (base on o.d. pulp). When a low peroxide charge of 0.5% was used at 60.0°C, the copper number was reduced by 39.5% and a 9.0% increase in fiber charge was observed. At 90.0°C, the same alkaline peroxide treatment resulted in lower fiber charge and intrinsic viscosity. The optimal temperature during peroxide treatment with respect to fiber charge was between 60°C and 70°C. Peroxide treatment of ECF bleached kraft pulp was compared with $NaBH_4$-reduced ECF bleached kraft pulp. The results for fiber charge and copper number indicate that carbonyl groups are the source of the elevated carboxyl group contents observed after peroxide treatment.

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